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LACTIC ACID DERIVATIVES AS PLASTICIZERS

ESTERS OF POLYMERIC LACTIC ACID

By

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It has been claimed that lactic acid, when manufactured on a large scale and under suitable conditions, can be made by fermentation at 10 cents a pound or less (19, 20) from several carbohydrate-containing raw materials. Some of these raw materials--whey (14, 21, 29, 31, 32, 33), molasses (20, 23), sulfite waste liquor (19), cull potatoes (8, 28), and citrus press liquors (22)--are readily available as wastes or byproducts, and their disposal presents serious economic and health problems. As part of a program aimed at finding new applications for lactic acid, esters of mixed lactic acid polymers (average degree of polymerization about three) were made and tested as plasticizers for a vinyl chloride resin, cellulose acetate, and ethyl cellulose. Particular attention was given to the evaluation of the lactic acid derivatives as plasticizers for vinyl chloride resins because of the large quantities of plasticizers now used with this type of resin. This paper describes the preparation and properties of the polylactic acid derivatives and gives the results obtained in evaluating these materials as plasticizers.

Plasticizers and the Plasticizer Industry

A plasticizer may be defined (5) as a liquid or low-melting solid that is added to synthetic resins or cellulose derivatives to modify a physical property such as flexibility, tensile strength, hardness, softening point, and adhesion. It may also affect other properties, such as gloss, water resistance, gas impermeability, fire resistance, oil resistance, and dielectric qualities. The primary purpose of any plasticizer, however, is to change the rate of deformation of the base resin so that, through the application of solvents, heat or pressure, useful products may be prepared by molding, calendering, casting, extruding, and other processes.

The rapidly growing plasticizer industry is a major new development of the organic chemical industry. Principally because of new markets for vinyl chloride resins, the annual requirement for plasticizers in the United States is now almost 200 million pounds (2, 3, 34). The demand for plasticizers should continue to parallel the growth of the plastics industry.

The production and consumption of synthetic resins, particularly those requiring plasticizers, have increased tremendously since 1939. Production of synthetic resins has increased from approximately 248 million pounds in 1939 to about 1-1/2 billion pounds in 1949 (5). At the same time, the requirements for plasticizers have increased from about 30 million to approximately

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200 million pounds. The vinyl resins alone now require about 100 million pounds of plasticizers a year. The rest is used with cellulose derivatives, rubber, synthetic rubber, chlorinated rubbers, and some thermoset resins (5).

The price of plasticizers ranges from about 15 to 90 cents a pound, based on current conditions; the average is approximately 35 cents. On the basis of these prices, the total plasticizer business is worth approximately \$70,000,000 annually (5).

Lactic Acid and Its Manufacture

The current annual production of lactic acid is about 4-1/2 million pounds (30). Since the sugar in molasses (20), sulfite waste liquor (19) and certain other byproducts is valued at less than 1 cent per pound, and the yields (both theoretical and actual) of lactic acid are high (24), the price of lactic acid should decrease when its production is expanded and manufacturing methods are improved. Table I indicates the availability of several potential raw materials for making lactic acid.

Table I. Carbohydrate raw materials potentially available for the manufacture of lactic acid.^a

Carbohydrate source	Annual production, million pounds		
	Raw material	Sugar	Potential lactic acid
Whey (1947) ^b	12,000	600	540
Waste liquor, sulfite and kraft pulp (1947) ^c	-	4,000	3,600
Hydrol ^d	200	150	135
Florida citrus molasses (1947-1948) ^e	132	53	47
Blackstrap molasses (1941) ^f	3,680	1,840	1,656

a. Production data are for the continental United States unless otherwise stated. A 90 percent yield of lactic acid is assumed for all the raw materials. Surplus potatoes and other surplus crops are omitted.

b. U. S. Department of Agriculture, Agricultural Statistics, 1947.

c. Holzer (15).

d. Production estimated by assuming that one part of hydrol is obtained in the manufacture of four parts of dextrose.

e. Iranzo, and Veldhuis (16).

f. Berdeshevsky (4).

Lactic acid has not received sufficient attention as a raw material in making plasticizers. For this use, it has the following advantages: (a) It is obtained in high yield by fermentation of relatively inexpensive raw materials such as starch hydrolyzates, whey, and molasses (24); (b) its production, unlike that of certain other chemicals, is not necessarily geared

to other commercial operations; (c) having two functional groups, it can be converted into many high-boiling derivatives having potential value as plasticizers; and (d) its derivatives have ester groups or other compatibilizing groups. Although the use of certain lactates (6,7) and polylactates (9, 10, 11) as plasticizers has been suggested, data on the merit of polylactates for this purpose apparently have not been published.

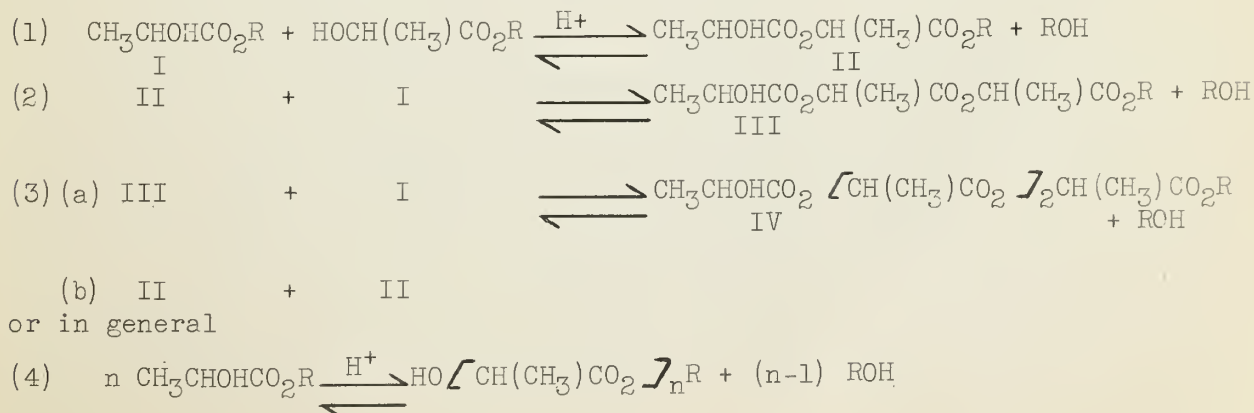
Preparation of Polylactates

The methods used to prepare the polylactates in the work reported here appear to be economical and more applicable to large-scale production than some previously described (9, 10, 11). Claborn prepared lactyllactates by alcoholysis of lactide (10), and subsequently acylated the lactyllactate (9). Others reported the reaction of alkyl lactates with α -acetoxypropionyl chloride to produce the desired lactyllactate derivatives (11). It should be pointed out, however, that neither lactide nor α -acetoxypropionyl chloride are commercially available raw materials.

The methyl, ethyl, and butyl esters of lactic acid, several primary and secondary alcohols, and an 82-percent edible-grade lactic acid were used as raw materials in making the polylactates (V, Equation 4) described in this paper. Esterification and alcoholysis methods were used to prepare them. The polylactates were acylated with an acid anhydride or chloride, usually after removal of alkyl lactate by vacuum distillation. The relatively volatile products were then removed by distillation under reduced pressure; the distillation residues, after treatment with alkaline agents to remove acidic components and with activated carbon to remove color, were tested as plasticizers.

Self-alcoholysis of alkyl lactates.--Lactic esters, $\text{CH}_3\text{CHOHCO}_2\text{R}$, are bifunctional, containing within the same molecule both hydroxyl and ester groups. Alcoholysis or ester interchange results from the interaction between these two functional groups. Because of their bifunctionality, self-alcoholysis of lactic esters results in a polymeric condensation product, which is a mixture of esters of polymeric lactic acid. Despite the extensive application of alcoholysis reactions (26), little has been published concerning the self-alcoholysis of lactic esters. Jungfleisch (17) heated ethyl lactate at 250°C . for 8 hours and found ethanol, ethyl lactate, ethyl lactyllactate, and lactide in the reaction mixture.

The reactions occurring in the self-alcoholysis, analogous to self-esterification of lactic acid (12), can be visualized by the following equations:



The self-alcoholysis of lactic esters occurs easily in the presence of catalysts, such as sulfuric and sulfonic acids, usually employed in esterification reactions. The reactions are reversible and attain an equilibrium; the equilibrium can be displaced by removal of alcohol from the reaction mixture.

Alkyl polylactates were made from methyl, ethyl, and n-butyl lactates by refluxing these alkyl lactates in the presence of a mineral acid catalyst while distilling the corresponding alcohol, that is, methanol, ethanol, or n-butanol. The reaction temperature was controlled by using appropriate pressures, and the degree of polymerization was governed by experimental conditions, especially the quantity of alcohol distilled from the reaction. The average degree of polymerization was approximately three. The viscosity values, however, suggest that the mixtures may be more complex. The method, described in detail under Experimental and in Table II, appears to be most applicable to the lower alkyl lactates, which are commercially available chemicals.

Undisturbed, the equilibrium mixture from methyl lactate approximated a 30-percent conversion to polylactate (Expt. 1, Table II). By distilling alcohol from the reaction mixture, however, conversions of 60-85 percent of the lactate resulted (Expts. 2-10, Table II). Conversions up to approximately 75 percent were readily obtained. The reaction became considerably slower at this point, and higher conversions were not so readily obtainable, at least under the conditions of our experiments. The yield based on ester groups was practically quantitative (see Table II); thus the average degree of condensation could be estimated from the amount of alcohol produced in self-alcoholysis.

Attempts were made to determine the composition of methyl polylactate by distillation (Vigreux still) of the reaction mixture at low pressure (approx. 1 mm.). Difficulty was encountered in collecting the polylactates higher than lactyllactate because of decomposition of the polylactate and crystallization of lactide at the still head and in the distillate. However, a partial analysis was obtained. Thus the reaction mixture of Experiment 3 (Table II) contained (by weight) 25 percent methyl lactate, 34 percent methyl lactyllactate, approximately 9 percent lactide, and 32 percent distillation residue (higher polylactates); or on a monomer-free basis, 45 percent methyl lactyllactate, approximately 12 percent lactide, and 43 percent higher polylactates. That the distillation residue can be considered as the methyl ester of higher polylactates was demonstrated by its conversion in high yield of methyl lactate (29 grams from 25 grams of residue) by treatment with methanol vapor as described in an earlier publication (13).

Mixed alcoholysis of alkyl lactates -- Attempts were made to prepare the polylactates of the higher alcohols by a method similar to the self-alcoholysis procedure in which 3 or more moles of methyl lactate were treated with 1 mole of a higher alcohol. Methanol was distilled from the mixture during the reaction. Although the purpose of this method was to prepare polylactates of the higher alcohol, the replacement of methyl by the higher alcohol

group under these experimental conditions was incomplete, thus resulting in a mixture containing methyl as well as higher alkyl polylactate. Hence this method was not considered suitable for the preparation of these polylactates.

Esterification.--This method, used principally for the preparation of the polylactates of the higher alcohols, consisted in esterifying 3 moles of aqueous 80-percent lactic acid with 1 mole of higher alcohol in the presence of a mineral acid catalyst. The reaction was conducted in vacuum for the purpose of removing the water already present and that formed by esterification, thus favoring the formation of the polylactate ester. Details of the procedure are given below under Experimental. Table III summarizes the preparation and properties of various higher alkyl and substituted alkyl polylactates.

The esterification procedure, in which a relatively pure grade of lactic acid was used, required less time and gave lighter colored products than the mixed alcoholysis procedure. The yields based on carboxyl and ester groups were almost quantitative. The polylactate ester, however, contained a relatively large amount of free acid, approximately 10 percent of the total available lactic acid remaining unesterified. It appears likely that this free acid could be greatly reduced by carrying out the esterification for a longer period of time.

These polylactates were acylated to esterify the remaining hydroxyl groups. An attempt was made to analyze n-octyl polylactate acetate by distillation at 0.05 mm in a tensimeter still (25). Figure 1 shows the distillation curve. Because of the low fractionation efficiency of the still (an alembic type), suitable analytical fractions were not obtained. An indication of the volatility behavior of the mixture can be drawn. Seventy percent of the mixture was distillable; approximately 15 percent distilled below the distilling temperature of butyl phthalate, 40 percent was intermediate with respect to butyl and octyl phthalate, and the remainder was higher boiling than octyl phthalate.

Experimental

Self-Alcoholysis of Alkyl Lactate

General procedure.--The following procedure for preparing butyl polylactate (Expt 9, Table II) is typical of this method. A mixture of 3675 grams (25 moles) of n-butyl lactate and 5 ml of concentrated sulfuric acid was placed in a flask containing a thermometer and a fine capillary air inlet tube to permit distillation in vacuum. The flask was attached to a 2-foot Vigreux column, and the system was operated under reduced pressure, 10-20 mm. The mixture was heated to 80-98° C and, maintaining reflux, the butanol was removed from the reaction as rapidly as formed, care being taken to adjust the take-off to maintain a vapor temperature of 40-45° C. After 18 hours, the rate of butanol formation had slowed considerably, and approximately 795 grams of distillate had been obtained. Then, without neutralizing the catalyst, the pressure was lowered to 10 mm, and unreacted butyl lactate was distilled from the reaction mixture, the pot temperature finally being raised to 110° C. This gave 1375 grams of distillate, and 1512 grams of butyl polylactate as brown, viscous residual liquid.

Table 11. Preparation and properties of alkyl poly lactates by self-alcoholysis of alkyl lactates^a

Expt. No.	Lactate, moles	Time, hrs.	Temp., °C.	Press., mm.	Conversion, %	ROH, moles/mole ^b	Polylactate					
							Equiv. wt. ^c	Yield ^d mole %	Viscosity cstks.	°C.	n _D ²⁰	d ₄ ²⁰
1	Methyl 4.0	4.0	114 ^e	760 ^e	50	0.43	-	-	-	-	-	
2	6.0	5.0	85-95	133	58	0.51						
3	10.0	8.5	do	do	79	0.61						
4	16.0	13.5	do	100	76	0.66	78.6	101	176.0	20°	1.4430 1.2043	
5	20.0	9.0	115-125	200-400	66	0.77	77.1	96			1.4501	
6	30.0	9.8	88-116	150	73	0.80	77.5	98	1304	40°	1.4480 1.2234	
7	Ethyl 4.0	10.8	85-95	95	68	0.68	84.4	96			1.4400 1.1695	
8		24.7	80-115	60	83	0.90	80.0	99	1094	40°	1.4460 1.2047	
9	n-Butyl 25.0	18.0	80-98	15	61	0.61	98.2	97	63	20°	1.4374 1.1003	
10		25.0	13.5	95-106	do	71	0.61	99.1	96			1.4360 1.1056
11	Methyl glycolate 2.0	1.3	116 ^e	760 ^e	26	0.66	71.8	94	-	-	-	

^a Catalyst was 0.20-0.25 ml. of concentrated H₂SO₄ per mole of ester except that in Experiment 9, which was 0.1 ml.^b Moles of alcohol produced per mole of ester consumed.^c Grams containing 1 equivalent of acid plus ester; free acid, mainly catalyst, was low, 1-2 mole percent.^d Calculated as moles of available lactic acid in polymer per 100 moles of lactate consumed.^e Refluxed (at atmospheric pressure) without removal of methanol; the temperature rapidly dropped to a constant value.

TABLE III. POLYLACTATES PRODUCED BY ESTERIFICATION OF 80-PERCENT LACTIC ACID WITH ALCOHOLS^a

Expt. No.	Polylactate	Temp., °C.	Time, hrs.	Press., mm.	Yield, mole %	Free Acid, % ^b	Equiv. wt. ^c	Properties		
								n _D ²⁰	d ₄ ²⁰	Viscosity at 20° C. cstks.
1 ^d	n-Butyl	70-130	2.7	95	99	7	84.0	1.4485	1.1684	341 (40°)
2	do	60-125	3.0	95	106	27	88.1	1.4441	1.1752	615
3	n-Octyl	44-110	4.8	25	101	5	114.9	1.4427	1.0517	89
4	do	45-120	7.5	25	99	21	113.9	1.4441	1.0598	131
5	do (CO ₂ atmos.)	50-130	5.0	30	81	-	133.4	1.4433	1.0581	115
6	2-Ethylhexyl	74-120	4.3	60	89	12	108.8	1.4444	1.0821	241
7	do	60-115	5.8	60	99	12	116.1	1.4427	1.0534	93
8	Capryl	55-118	7.5	45-60	99	5	108.9	1.4418	1.0197	222
9	Benzyl	59-130	4.0	50-70	102	14	108.2	1.4890	1.1843	545
10	2-Ethoxyethyl	52-79	6.0	60	99	11	90.3	1.4471	1.1904	2721
11	2-Butoxyethyl	60-120	6.0	60	100	31	110.3	1.4420	1.1225	137
12	2-Phenoxyethyl	55-135	6.5	60	97	8	120.0	1.4919	1.1998	2598
13	2-(2-Butoxyethoxy) ethyl	60-150	3.5	54	98	2	126.9	1.4470	1.1151	121

^a Catalyst was 0.20-0.24 ml. of concentrated H₂SO₄ per mole of lactic acid. Mole ratio lactic acid: alcohol = 3.^b Expressed as equivalents of free acid per 100 equivalent of acid plus ester.^c Grams containing 1 equivalent of acid plus ester, determined by saponification.^d Catalyst was p-toluenesulfonic acid monohydrate, 1.4 grams per mole.

Redistillation of the volatile material resulted in isolation of 708 grams (9.57 moles) of butanol and 1412 grams (9.67 moles) of butyl lactate. The conversion was 61 percent, and the yield--on an equivalent basis--was 97 percent. The free acid of the polylactate was only 1.5 percent of the total available lactic acid.

Table II summarizes the preparation of other polylactates by self-alcoholysis of the lactic ester and some of their properties. In the preparation of methyl polylactate, ice water was circulated in the condenser to insure condensation of methanol, which boiled at 37° C. under the pressure (133 mm.) employed in the alcoholysis reaction. Obviously the pressure at which the alcohol was removed determined the temperature of alcoholysis and could be varied over a wide range. In these experiments, it was preferred to operate at a pressure that would produce a reaction temperature of approximately 100° C.

Esterification of Lactic Acid to Produce Polylactates

The procedure was essentially that described here for the preparation of n-octyl polylactate (Expt. 4, Table III). A mixture of 2310 grams (21 moles) of aqueous 81.7 percent lactic acid, 910 grams (7 moles) of n-octyl alcohol, and 5 ml. of concentrated sulfuric acid was placed in a flask containing a thermometer and a fine capillary to permit distillation in vacuum. The flask was attached to a Vigreux column, and the system was operated at a pressure of 25 mm. The reaction mixture was heated to reflux, and water was distilled from the reaction mixture. The vapor temperature was 27-31° C., and the reaction temperature, initially 45° C., rose to 120° C. in 7.5 hours.

The distillate consisted of 780 grams of water and 20 grams (2 percent of input) of octyl alcohol.

The reaction mixture was then topped at 1-2 mm. while being heated at approximately 130° C. for 4 to 5 hours; 267 grams of n-octyl lactate was collected. The n-octyl polylactate (2210 grams) remained as a brown liquid. When the reaction and removal of volatile products were carried out in an inert atmosphere, carbon dioxide instead of air, a considerably lighter colored product was obtained.

When a relatively volatile alcohol such as butyl (Expts. 1 and 2, Table III) was used in the esterification, the vapors were led to a Barrett-type Dean and Stark moisture trap. This permitted separation of butanol from the water and return of the alcohol to esterification mixture.

Acyl Derivatives of Polylactates

Acylation with anhydrides.--The polylactate was heated with an excess of acetic or propionic anhydride for 4-5 hours on a steam bath. The mixture was topped free of acid and anhydride by heating it at 1 mm. to a final pot temperature of approximately 125° C. The residue was washed several times with water, then with sodium bicarbonate solution. When trouble with emulsions was encountered, salt was added to the wash solutions. The organic layer was dried by evaporation of the water at 1 mm. (final pot temperature approximately 100° C.). The product was then decolorized with activated carbon (approximately 5 percent).

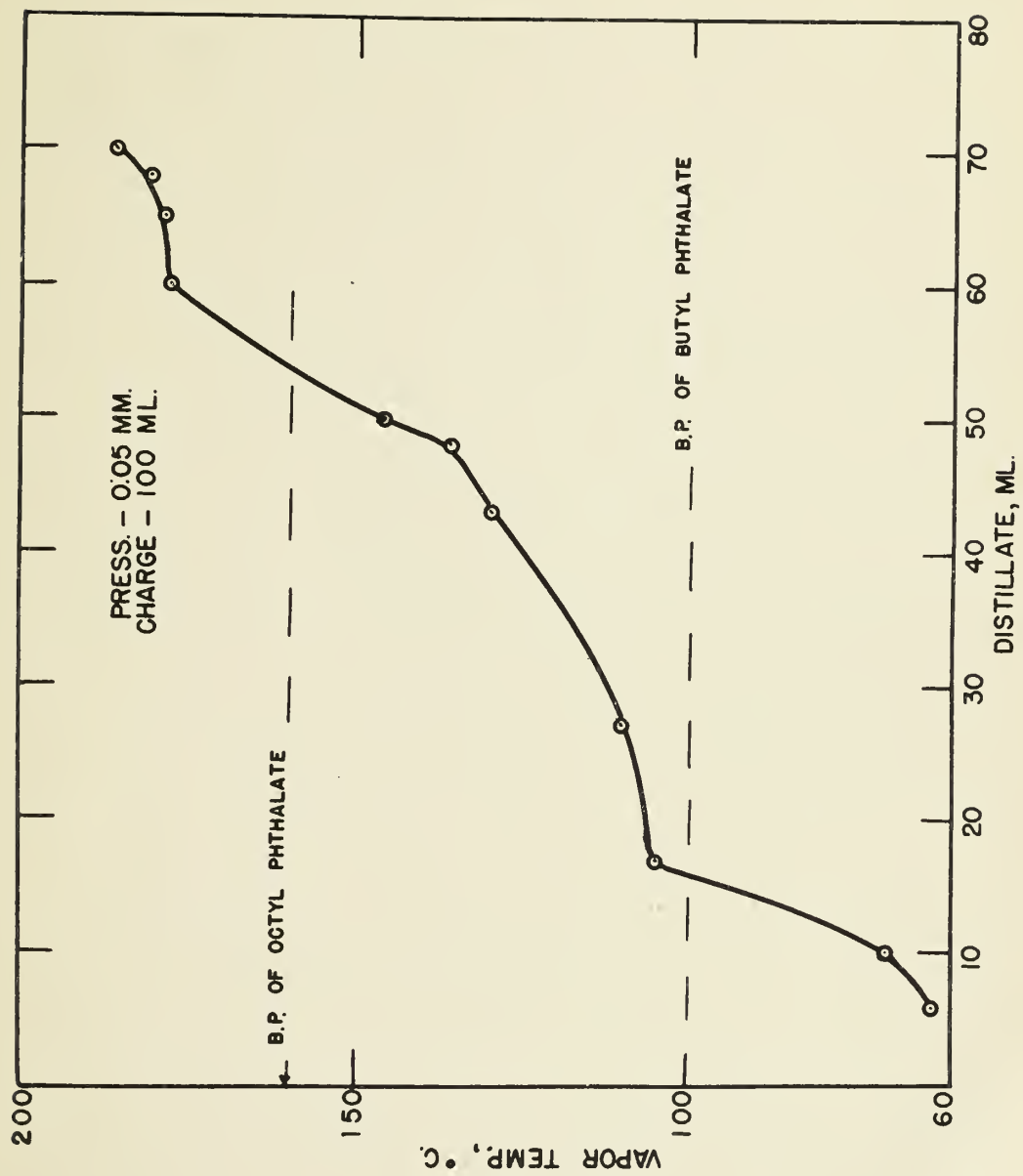


FIG.1 DISTILLATION OF n-OCTYL POLYLACTATE ACETATE

Acylation with acid chlorides.--The other acyl derivatives were prepared by acylation with the acid chloride. The polylactate was dissolved in a slight excess of pyridine, and an inert solvent such as benzene or toluene was added. The acid chloride was added slowly to the stirred solution, and the reaction temperature was maintained at approximately 20° C. After standing overnight, the reaction mixture was poured into water and washed as described above. The benzene or toluene solution was then freed of solvent and water simultaneously by evaporation at 1 mm.

Table IV lists the various acyl derivatives and their properties.

Evaluation of Plasticizers

Compatibility.--An acetone solution of cellulose acetate and the plasticizer was poured on a glass plate. Upon slow evaporation of the solvent, a film of the plasticized composition was obtained, which was then heated for 4 hours at 60° C. A clear film indicated compatibility.

Compatibility in ethyl cellulose was determined as described above under cellulose acetate, except that a toluene-ethanol (80:20) mixture was used as the solvent. The concentration of plasticizer in the plasticized cellulose plastics was 20-25 percent.

Compatibility in polyvinyl chloride was determined by milling the plasticizer with Vinylite VYDR², a 95-percent vinyl chloride-5-percent vinyl acetate copolymer, and observing the molded sheets after conditioning (18).

Testing polyvinyl chloride composition.--The milling and molding procedure was essentially that described in a technical bulletin (1). The formulation used was:

	Parts
Polyvinyl chloride (VYDR)	63.5
Basic lead carbonate	1.0
Stearic acid	0.5
Plasticizer	35.0

The molded sheets (6 x 6 x 0.08 inches) were conditioned for 24-48 hours at 77° F. and 50 percent relative humidity. Dumbbell test specimens with necks 0.125-inch wide and 1-inch long in the straight portion were die-cut from the molded sheet, and conditioned for 1 hour at 70° F. and 65 percent relative humidity. The tensile strength, 100 percent modulus, and elongation were determined (70° F., 65 percent relative humidity). A Scott IP-4 tester was used, and the rate of load application was 73 pounds per minute. Specimens, 1/4 x 1-1/2 inch, were cut from the molded sheet for determination of the brittle point by the method of Kemp (27). The results are summarized in Table V.

² THE MENTION OF SPECIFIC BRANDS IS NOT AN ENDORSEMENT OR RECOMMENDATION OF THESE PARTICULAR BRANDS OVER THOSE NOT MENTIONED.

Table IV. Properties of acyl derivatives of alkyl polylactates

Acyl polylactate	n_D^{20}	d_4^{20}	Viscosity at 20°C, cstks.	Free acid, % ^a	Equiv. wt. ^b	Compatibility ^c	
						Cellulose acetate ^d	Ethyl cellulose ^e
Methyl polylactate acetate	1.4391	1.1907	3050	1.0	72.0	C	C
Methyl polylactate propionate	1.4431	1.1170	1047	10.3	75.1	C	C
Methyl polylactate laurate	1.4447	1.0363	194		107.3	I	C
Methyl polylactate benzoate	1.4830	1.2223	7170 (40°)	5.6	83.0	I	SI
Methyl polylactate DGC ^f	1.4507		1659 (40°)	2.6	77.9	C	C
Ethyl polylactate acetate	1.4444	1.1974	2098 (40°)	1.2	74.1	C	C
Ethyl polylactate propionate	1.4364	1.1435	252	0	78.0	C	C
Ethyl polylactate laurate	1.4469	1.0729	1606	2.8	96.4	I	C
Ethyl polylactate n-hexyl carbonate	1.4440	1.0418	7061	2.4	87.7	I	C
Butyl polylactate acetate	1.4328	1.1103			83	C	C
Butyl polylactate propionate	1.4352	1.0084	73	4.3	86.3	C	C
Butyl polylactate 2-ethylhexoate	1.4380	1.0256	49	4.0	119.9	I	SI
Butyl polylactate laurate	1.4442	0.9915	56	6.0	124.0	I	SI
Butyl polylactate benzoate	1.4825	1.1291	346	0	97.8	I	C
Butyl polylactate DGC ^f	1.4489	1.1820	461 (40°)	0.7	101.5	C	C
Butyl polylactate n-hexyl carbonate	1.4368	0.9099	85	0	105.5	I	C
Butyl polylactate n-octyl carbonate	1.4390	0.9305	76	0	113.8	I	C
n-Octyl polylactate acetate	1.4390	1.0631	80	<1	95.0	I	C
n-Octyl polylactate propionate	1.4394	1.0496	77	<1	98.0	I	C
n-Octyl polylactate pelargonate	1.4434	1.0069	73	4.0	115.8	I	C
n-Octyl polylactate benzoate	1.4771	1.0888	315	2.0	107.5	SI	C
n-Octyl polylactate DGC ^f	1.4508	1.1183	3756	1.5	102.9	I	C
2-Ethylhexyl polylactate acetate	1.4370	1.0350	33	2.0	101.2	SI	C
2-Ethylhexyl polylactate propionate	1.4360	1.0094	18	0.8	108.2	I	C
2-Ethylhexyl polylactate 2-ethylhexoate	1.4421	1.0028	75	16.6	134.1	I	C
2-Ethylhexyl polylactate laurate	1.4460	0.9632	50	11.0	125.6	I	C
2-Ethylhexyl polylactate benzoate	1.4819	1.0352	203	11.0	114.0	SI	C
2-Ethylhexyl polylactate DGC ^f	1.4503	1.1115	2149	0.7	89.6	SI	C

Capryl poly lactate acetate	1.4398	1.0807	515	1.5	89.4	I
Capryl poly lactate laurate	1.4449	0.0978	121	4.0	126.1	I
Capryl poly lactate n-hexyl carbonate	1.4400	1.0242	171	.5	118.9	I
Benzyl poly lactate acetate	1.4809		78	9.0	92.2	-
Benzyl poly lactate propionate	1.4858	1.1413	94	2.0	104.0	C
Benzyl poly lactate pelargonate	1.4794	1.0828	205	6.0	125.0	C
Benzyl poly lactate benzoate	1.5109	1.1805	959	20.1	111.1	C
Benzyl poly lactate DGC ^f	1.4902		5210 (40°C)	1.0	102.5	C
2-Ethoxyethyl poly lactate propionate	1.4423	1.1623	1046	14.4	87.6	C
2-Ethoxyethyl poly lactate n-amyl carbonate	1.4381	1.1103	122	15.1	101.5	C
2-Butoxyethyl poly lactate acetate	1.4347	1.1154	88	14.0	87.0	C
2-Phenoxyethyl poly lactate acetate	1.4808	1.1896	2468	4.0	98.2	C
2-Phenoxyethyl poly lactate propionate	1.4795	1.1686	906	3.0	102.0	C
2-Phenoxyethyl poly lactate benzoate	1.5153	1.0981	767 (40°C)	2.0	111.6	C
2-Phenoxyethyl poly lactate DGC ^f	1.4933	1.2405	8206 (40°C)	2.0	108.2	C
2-(2-Butoxyethoxy)-ethyl poly lactate acetate	1.4415	1.1092	116	1.0	102.8	C
2-(2-Butoxyethoxy)-ethyl poly lactate propionate						
2-(2-Butoxyethoxy)-ethyl poly lactate laurate	1.4410	1.0070	84	4.5	102.4	C
2-(2-Butoxyethoxy)-ethyl poly lactate benzoate	1.4480	0.9101	99	3.3	146.3	I
2-(2-Butoxyethoxy)-ethyl poly lactate DGC ^f	1.4785	1.0279	471	7.0	120.7	C
	1.4533	1.1652	3357	2.4	115.4	C

^a Expressed as equivalents of free acid per 100 equivalent of acid plus ester.

^b Determined by saponification and includes free acidity.

^c C = compatible; I = incompatible; SI = borderline compatible.

^d Hercules Powder Co's FN-6. Plasticizer, 20-25 percent.

^e Hercules Powder Co's N-100. Plasticizer, 20-25 percent.

^f DGC = diglycol bis-carbonate.

Table V. Properties of polyvinyl chloride (VYDR) compositions plasticized with polylactate^a

Plasticizer	Compatibility ^b		Tensile strength, psi	Modulus (100%), psi	Elongation %	Brittle point, °C.
	Unaged ^c	Aged ^d				
Methyl polylactate acetate	I		Could not be milled			
Methyl polylactate propionate	I		do			
Methyl polylactate laurate	I		do			
Methyl polylactate benzoate	I		do			
Ethyl polylactate acetate	I		3660	2660	300	-5
Ethyl polylactate laurate	C	I	3150	2330	320	+22
Ethyl polylactate n-hexyl carbonate	C	I	3210	2720	300	-5
Butyl polylactate acetate	C		3630	2570	230	-5
Butyl polylactate propionate	C		3520	2200	250	-5
Butyl polylactate 2-ethylhexoate	SI	I	3360	1890	280	-15
Butyl polylactate laurate	SI		3110	1780	290	-30
Butyl polylactate benzoate	SI		3600	2480	270	+5
Butyl polylactate diglycol carbonate	C	I	3750	3120	300	+8
Butyl polylactate n-hexyl carbonate	C	I	3110	1750	290	-8
Butyl polylactate n-octyl carbonate	C	I	3520	1580	300	-36
n-octyl polylactate acetate	C		3500	1990	290	-8
n-octyl polylactate propionate	C		3410	1910	280	-14
n-octyl polylactate pelargonate	C		3060	1820	270	-25
n-octyl polylactate benzoate	C	I	3680	2360	290	-3
n-octyl polylactate diglycol carbonate	C	I	3460	2670	280	+4
2-Ethylhexyl polylactate acetate	C	C	3780	2190	270	-10
2-Ethylhexyl polylactate propionate	C	C	3270	2030	290	-23
2-Ethylhexyl polylactate 2-ethylhexoate	C	I	3380	1760	360	-25
2-Ethylhexyl polylactate laurate	I		Could not be milled			
2-Ethylhexyl polylactate benzoate	C	SI	3690	2300	250	-2
2-Ethylhexyl polylactate diglycol carbonate	C	I	3620	2820	260	+14

Capryl poly lactate acetate	C	I	3430	2410	280	+1
Capryl poly lactate laurate	I			Could not be milled		
Capryl poly lactate n-hexyl carbonate	C	I	3660	2140	330	-10
Benzyl poly lactate acetate	I		3890	2450	280	-6
Benzyl poly lactate propionate	I		3680	2190	300	-3
Benzyl poly lactate pelargonate	I			Could not be milled		
Benzyl poly lactate benzoate	C		3880	3230	215	+4
Benzyl poly lactate diglycol carbonate	I			Could not be milled		
2-Ethoxyethyl poly lactate propionate	I					
2-Ethoxyethyl poly lactate n-amyl carbonate	C	I	3660	2700	300	-2
2-Butoxyethyl poly lactate acetate	I		3460	3180	240	+14
2-Phenoxyethyl poly lactate acetate	I		3330	2980	300	+1
2-Phenoxyethyl poly lactate propionate	I		3260	2670	260	-3
2-Phenoxyethyl poly lactate benzoate	SI	I	3810	3580	230	+14
2-Phenoxyethyl poly lactate diglycol carbonate	I			Could not be milled		
2-(2-Butoxyethoxy)-ethyl poly lactate acetate	I		3390	1820	330	-16
2-(2-Butoxyethoxy)-ethyl poly lactate propionate	I		3390	1690	330	-21
2-(2-Butoxyethoxy)-ethyl poly lactate laurate	I		2570	1760	210	-17
2-(2-Butoxyethoxy)-ethyl poly lactate benzoate	SI	I	3710	2230	320	-7
2-(2-Butoxyethoxy)-ethyl poly lactate diglycol carbonate	I					
Control: DOP	C	C	5070	1500	290	-32

^a Contained 35% plasticizer.

^b C = compatible; I = incompatible; SI = borderline compatibility.

^c Molded composition after conditioning at 70°F. for 24 to 48 hours.

^d After several months at room temperature.

Discussion of Results

Polylactic acid may be thought of as an hydroxy acid in which the hydroxyl and carboxyl functions are separated by intervening ester groups. Though many derivatives of lactic acid have been reported, little has been published concerning derivatives of polylactic acid. In this paper, polylactates, esters of the carboxylic function of polylactic acid, have been prepared by two commercially attractive processes, namely, (a) self-alcoholysis of lactic esters, and (b) esterification of an alcohol with an excess (100 mole percent or more) of lactic acid.

The polylactates, containing an hydroxyl group, were capable of being acylated to form derivatives of the type $\text{RCOO} \left[\text{CH}(\text{CH}_3) \text{COO} \right]_n \text{R}'$. The derivatives prepared were those of the low molecular weight polylactates, where n has an average value of three.

These reactions do not result in a single pure ester but in a mixture of several closely related esters. For application as a plasticizer, a single pure compound is not of prime importance, blends often being used. It would be important, however, to attain a mixture of constant composition. The reactions being reversible, an equilibrium mixture of polylactate esters could be attained, which should be reproducible.

Regarding plasticizing properties, practically all these polylactate derivatives at 20-25 percent concentration were compatible with ethyl cellulose (Table IV). In general, the derivatives of methyl, ethyl, benzyl, 2-ethoxyethyl, 2-butoxyethyl, 2-phenoxyethyl, and 2-(2-butoxyethoxy)-ethyl polylactate, as well as the acetate and propionate of butyl polylactate at 20-25 percent concentration were compatible with cellulose acetate (Table IV).

Upon first examination, many of these polylactate derivatives appeared to be compatible with VYDR, a 95-percent vinyl chloride copolymer. Upon long standing, however, the plasticizer exuded from most of these compositions. Thus these materials do not appear to be suitable as primary plasticizers for this plastic. In efficiency, as judged by 100 percent modulus and brittle point, only the laurate and the octyl carbonate of butyl polylactate approached that of DOP (Table V).

Several of the grossly incompatible polylactate derivatives when blended with 50 percent by weight of DOP resulted in polyvinyl chloride compositions which were compatible even after several months of aging. As shown in Table VI, the blend of capryl polylactate laurate with DOP appeared to be approximately equal to DOP in efficiency.

Summary

Methyl, ethyl, and butyl polylactates were prepared by the self-alcoholysis of methyl, ethyl, and butyl lactates in the presence of a mineral acid catalyst. The polylactates of higher alcohols, that is, octyl, 2-ethylhexyl, capryl, benzyl, 2-ethoxyethyl, 2-butoxyethyl, 2-phenoxyethyl, and 2-(2-butoxyethoxy)-ethyl polylactates were obtained by esterification of 3 moles of

Table VI: Properties of polyvinyl chloride compositions plasticized with polylactate - DOP blends (50-50)^a

Polylactate Blend	Compatibility		Tensile strength psi	Modulus (100%), psi	Elongation, %	Brittle point, °C.
	Unaged	Aged ^d				
Capryl polylactate laurate	C	C	3410	1650	320	-30
Benzyl polylactate propionate	C	C	3410	1550	320	-15
Benzyl polylactate pelargonate	SI	C	3540	1830	340	-19
2-Ethoxyethyl polylactate propionate	C	SI	3470	1670	340	-8
2-(Butoxyethoxy)-ethyl polylactate acetate	C	I	3200	1550	310	-18
2-(Butoxyethoxy)-ethyl polylactate propionate	C	I	3260	1440	330	-28
2-(Butoxyethoxy)-ethyl polylactate laurate	C	I	3260	1430	370	-32
2-(Butoxyethoxy)-ethyl polylactate benzoate	C	C	3600	1720	330	-16.
Control DOP	C	C	3070	1500	290	-32

^a Contained 35 percent plasticizer.

^b C = compatible; I = incompatible; SI = borderline compatibility.

^c Samples conditioned for 24 to 48 hours.

^d Several months' storage at room temperature.

80-percent lactic acid with 1 mole of alcohol. The polylactates were of low molecular weight, that is, approximately three lactic acid units (average) in the chain. The acetates, propionates, 2-ethylhexoates, pelargonates, laurates, benzoates, diglycol bis (carbonates) and alkyl carbonates of the various polylactates were formed by acylation. Most of the derivatives described were compatible with ethyl cellulose and approximately half were compatible with cellulose acetate. While most of the esters do not appear suitable as primary plasticizers for vinyl chloride polymers, they can be used as 50-50 blends with certain commercial plasticizers.

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